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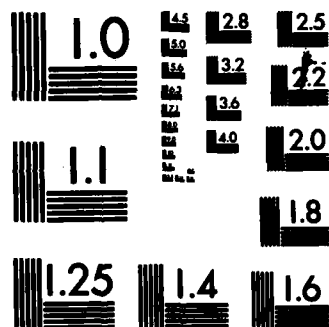
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Preparation and Properties of Transition Metal Beta'' Aluminas

by

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Prepared for Publication in
Solid State Ionics

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ion exchange techniques were used to produce a family of 3d transition metal B"-alumina single crystals. Complete or nearly complete replacement was obtained for Cr ³⁺ , Mn ²⁺ , Co ²⁺ and Ni ²⁺ compositions. Optical properties of the crystals were studied and both broad absorption and broad fluorescence bands were observed. Environmental exposure produced detrimental effects over long time periods, suggesting hydration of the conduction planes.		

PREPARATION AND PROPERTIES OF TRANSITION METAL β'' ALUMINAS

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Ion exchange techniques were used to produce a family of 3d transition metal β'' -aluminas by substitution of the sodium ion content in Na^+ - β'' -alumina single crystals. Complete or nearly complete replacement was obtained for Cr^{3+} , Mn^{2+} , Co^{2+} , and Ni^{2+} compositions. Optical properties of the crystals were studied and both broad absorption and broad fluorescence bands were observed. Environmental exposure produced detrimental effects over long time periods, suggesting hydration of the conduction planes.

1. INTRODUCTION

Previous studies^{1,2} have found that the entire sodium ion content of β'' -alumina can readily be replaced by a variety of divalent and trivalent cations. In several cases, it has been found that the resultant materials have interesting optical properties in addition to fast ion transport. For example, Nd^{3+} exchanged β'' -alumina single crystals have been found to lase and to exhibit extremely high fluorescent gain coefficients in comparison with $\text{Nd}:\text{YAG}$ lasers.³

The research on lanthanide β'' -aluminas prompted our interest in the 3d-transition metals as candidates for exchange into β'' -alumina. Several ions within this series exhibit broadband, vibronic fluorescent transitions due to the interaction of their incomplete 3d electron shells with local crystal fields. This phenomenon allows for the development of tunable solid state lasers using various oxide and non-oxide host materials. Relatively little work has been done, however, with β'' -alumina systems

in which the exchanged ions were capable of multiple valence states. In addition to this problem, the exchange of transition metal ions generally involves the substitution of ions with very small radii, potentially inducing large stresses within the crystals. The preparation of these materials, and their interesting optical properties are reported in this paper.

2. PREPARATION OF THE MATERIALS

Several transition metal β'' -aluminas were prepared using standard ion exchange techniques on single crystals of Na^+ - β'' -alumina (Table 1). Crystals were either immersed in molten halide salts of appropriate compositions or placed in the proximity of heated, but unmelted, salts for varying times. In this latter case the salt exhibited a sufficiently high vapor pressure such that ion exchange occurred from exposure to the vapor phase. For all samples, careful atmospheric control was required to prevent oxidation of the halide salts as well as to prevent

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TABLE 1: Ion Exchange Conditions for Transition-Metal- β' -Aluminas

ION	EXCHANGE MEDIUM	TEMPERATURE(°C)	TIME(hr)	PERCENT EXCHANGED
Cr^{3+}	Liquid: $31\text{CrCl}_3/69\text{NaCl}$	700	1	30
	Vapor: CrCl_3		12	90
Mn^{2+}	Liquid: MnCl_2	650	15	100
Co^{2+}	Liquid: CoCl_2	750	2	100
Ni^{2+}	Liquid: $32\text{NiCl}_2/68\text{NaCl}$	700	12.5	25
	Vapor: NiCl_2		35	90

formation of multiple valence states of the cations.

Results indicate that substantial or complete exchange was attained for Cr^{3+} , Mn^{2+} , Co^{2+} , and Ni^{2+} using both the liquid and vapor phase techniques. The crystals possess good mechanical integrity and x-ray diffraction indicates that the β' -alumina structure was retained without modification, despite the small size of the substitutional ions. The extent of the exchange reactions was monitored by both gravimetric means and Energy Dispersive X-ray (EDX) analysis, the latter also being used to identify impurities and inhomogeneities in the crystal.

The vapor phase exchanges, achieved by either burying the crystal in an excess of the halide powders or by suspending it above the powder source, required longer reaction times than corresponding melt exchanges. This method, however, enables one to obtain complete exchange at much lower temperatures than those required for the melt phase. In general, the resulting milder synthesis conditions prevent detrimental effects to the crystal. For example, complete exchange of Ni^{2+} ions from a melt of NiCl_2 would require melting the salt in excess of 1100°C , while the vapor phase exchange was possible at 700°C . This temperature reduction is critical, for it has been shown that several of the

exchanged β' -aluminas are prone to decomposition when heated to temperatures of above 900°C .⁴

3. OPTICAL PROPERTIES

Although most lasers operate at single wavelengths, the success of the room temperature operation of the $\text{Cr}:\text{BeAl}_2\text{O}_4$ (alexandrite) tunable laser, operational over the range for 7300 to 8000Å, has spurred much interest in the utilization of broad band vibronic transitions. Most radiative transitions within the 3d transition metal ions take place via such broad bands, and thus, there is the potential for a whole series of solid state lasers that are tunable over large wavelength regions. Numerous studies of transition metal ions in various crystal hosts have taken place. Although there is a wealth of spectroscopic information, there are relatively few effective laser hosts available. Our initial experiments were performed with the intent of determining the applicability of β' -alumina as a host for tunable solid state lasers, in that it has already demonstrated success as a laser host for Nd^{3+} ions.

Absorption and fluorescence spectra for several single crystals of ion exchanged β' -alumina with various Cr^{3+} concentrations (the balance being residual Na^+ ions within the conduction plane) were performed. The absorption

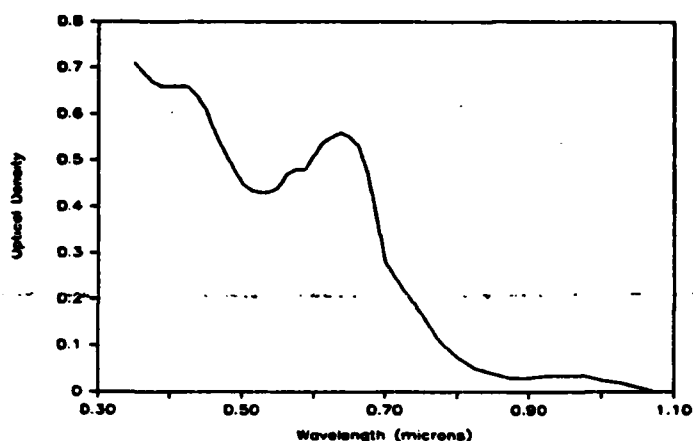


Figure 1. Absorption Spectrum of Cr^{3+} - β' -alumina.

spectra were obtained using a Cary Model 14 spectrophotometer. Cr^{3+} - β' -alumina was found to have strong absorption peaks centered at 4200Å and 6400Å (Fig. 1), giving the crystals a deep green color. Fluorescent emission (induced by pumping with a Spectra-Physics argon ion laser at 4880Å) was observed from 6900Å to 9000Å. These values are quite typical of Cr^{3+} optical spectra in a variety of other hosts, representing interaction between the 4T_1 (at 4200Å) and 4T_2 (at 6400Å) states with the vibronically broadened ground state 4A_2 . No evidence of the parity and spin forbidden ${}^2E \leftrightarrow {}^4A_2$ transition is observed, probably due to overlap of the 2E state with the 4T_2 . The placement of these transitions suggests that the local crystal field environment of the Cr^{3+} ions within the β' -alumina conduction plane is octahedral, which could place them within the mid-oxygen (mO) cation of the crystal.

The absence of the 2E line suggests that the magnitude of the crystal field environment in Cr^{3+} - β' -alumina is similar to that of Cr^{3+} in SGG [$\text{Ga}_2(\text{Sc,Ga})_2\text{Ga}_3\text{O}_{12}$], which has an octahedrally symmetric Cr^{3+} site with a crystal field of $Dq = 1450 \text{ cm}^{-1}$ and a Racah parameter $B = 658 \text{ cm}^{-1}$ ($Dq/B = 2.20$).⁵ This produces

a direct overlap of the 2E and 4T_2 levels.

However, the observed room temperature fluorescent lifetimes of the β' -alumina crystals is much greater than that observed in GSGG (650 versus 115 microseconds). This trend usually suggests that there is a greater separation between the 2E level, which typically has lifetimes of several milliseconds, and the 4T_2 level, whose lifetime is measured in the tens of microseconds. Given that we observe a lifetime greater even than that of alexandrite (262 microseconds at room temperature)⁶, it would suggest a larger crystal field than concluded above, more on the order of $Dq/B = 2.5$.⁷

The temperature dependent behavior of the fluorescent lifetime of Cr^{3+} - β' -alumina fails to provide any explanation for these contradictory observations. The lifetimes are found to decrease exponentially with increasing temperature, inferring the presence of some competing non-radiative process. A plot of the non-radiative decay rate versus inverse temperature (Fig. 2) indicates that the process has an activation energy of 0.16 eV, which is of the same order of that for sodium ion motion in this temperature range.⁸ While it is tempting to associate the non-radiative processes with Na^+

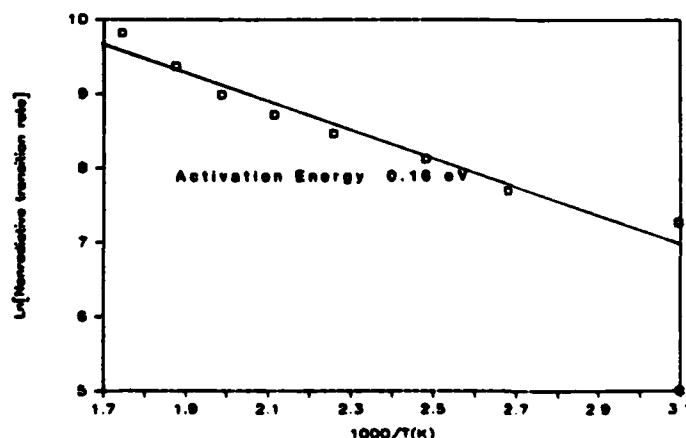


Figure 2. Non-radiative decay rate in Cr^{3+} - β' -alumina versus temperature.

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ion motion, there may be other competing non-radiative processes, such as multi-phonon decay, and partitioning via Boltzmann distributions between the closely lying 2E and 4T_2 levels.⁶ More detailed optical and ion transport studies are necessary in order to understand the non-radiative mechanisms occurring in this solid electrolyte.

In addition to the above effects there also seem to be other processes which contribute to the observed values of fluorescent lifetimes in these crystals. Concentration quenching has been observed, as increasing amounts of Cr^{3+} ions within the conduction plane have been found to reduce the lifetime by more than an order of magnitude (Fig. 3). Another quenching effect on the fluorescent lifetime occurs from the exposure of the crystals to ambient environments over long periods of time. For example, a crystal whose lifetime immediately after exchange was as high as 2 msec was found to degrade to 300 microseconds after prolonged ambient exposure (i.e., months). The process was found to be at least somewhat reversible. Heating the crystal to 350°C for 48 hours raised the lifetime to 650 microseconds.

Elevated heating was also found to affect

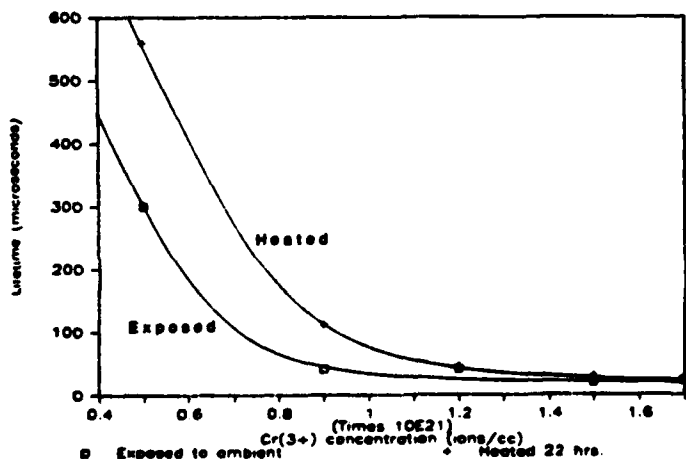


Figure 3. Fluorescent lifetime of $Cr-\beta'$ -alumina versus Cr concentration in hydrated and dried states.

the size of the c-axis lattice parameter of the crystals. In the unheated (short lifetime) state, a c-axis value of 33.666Å was measured, whereas after 48 hours of heating, the value was 33.547Å. The ability of water molecules to diffuse into β' -alumina and alter their lattice parameters is well established.⁹ In addition, water is well known for its ability to quench fluorescence over a wide variety of energies due to its many vibrational and bending modes. The present results indicate that certain optical properties may be sensitive to moisture. A more controlled study of this behavior is necessary to identify and characterize these effects.

The absorption spectra for Co^{2+} ion exchanged β' -alumina was also measured (Fig. 4), revealing strong peaks at 5500, 5825, and 6200Å, and lesser, but still strong, absorptions at 12,500, 13,625 and 15,250Å. The position of these peaks is in excellent agreement with the results reported for Co^{2+} in various oxide hosts containing tetrahedral sites.¹⁰ This indicates that the primary location of the Co^{2+} ions is the tetrahedral Beavers-Ross type site (6c), despite the fact that most divalent ions in β' -alumina exhibit significant population of both the BR and mid-oxygen sites.¹¹

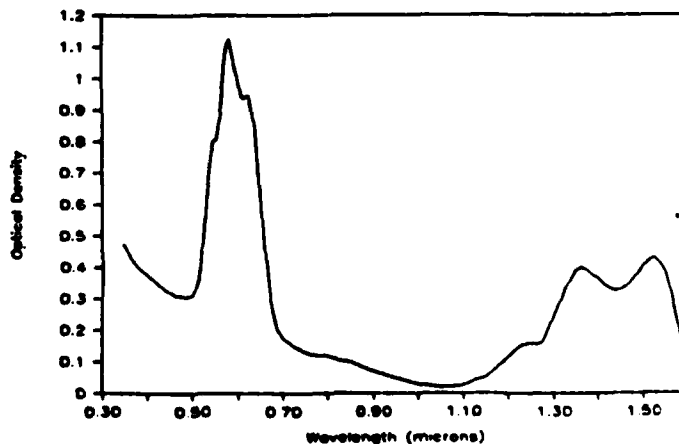


Figure 4. Absorption Spectrum of $Co^{2+}-\beta'$ -alumina.

The excellent agreement with the theoretical line positions, as well as the absence of any unidentified lines helps to verify that all the cobalt ions present in the crystal are in the $2+$ state, and that no Co^{3+} ions were formed during the exchange process.

Absorption spectra for Ni^{2+} - β' -alumina (Fig. 5) produces peaks at 3760, 6000, 6375, 7200 and 11,500Å. This latter absorption is positioned similarly to the absorption due to the first excited state of Ni^{2+} in MgO .¹² However, the complexity of the spectra and the sensitivity of the Ni^{2+} ion to crystal fields prevents the identification of the other lines in the spectrum. Low temperature measurements will be necessary to resolve some of the overlapping and determine crystal field strength and site symmetry.

4. CONCLUSION

The preparation of a new family of β' -alumina by the substitution of 3d transition metal ions for Na^+ ions has enabled us to begin investigating a new series of materials with potential as solid state tunable lasers. The optical properties of these materials compare favorably with those of materials previously

studied, and the vast benefits of ion exchange as a preparation technique permit the synthesis of many samples covering a wide variety of active ion concentrations. Initial results with Cr^{3+} exchanged β' -alumina indicate that hydration effects may influence the optical properties of this material.

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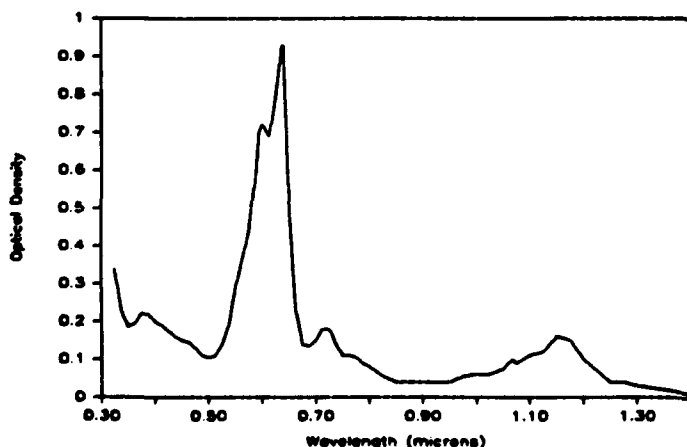


Figure 5. Absorption Spectrum of Ni^{2+} - β' -alumina.

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